

Comparison of Pb–Sm–Sn and Pb–Ca–Sn alloys for the positive grids in a lead acid battery

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Abstract

The anodic behavior of Pb–0.73 wt.% Sm–0.63 wt.% Sn and Pb–0.088 wt.% Ca–0.63 wt.% Sn alloys in sulfuric acid solution has been studied using linear sweep voltammetry, impedance–time curves and cyclic voltammetry. The experimental results show that the samarium in the Pb–Sm–Sn alloy can inhibit the growth of the anodic corrosion layer (PbO_2) formed on the alloy. Moreover, the rate of the oxygen evolution at the Pb–Sm–Sn alloy electrode is lower than that at the Pb–Ca–Sn alloy electrode. 2V–200Ah VRLA batteries were separately manufactured using the Pb–Sm–Sn and Pb–Ca–Sn positive grids. The results of the test show that the capacity loss of the battery with the Pb–Sm–Sn positive grids is significantly less than that of the battery with the Pb–Ca–Sn positive grids.

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1. Introduction

So far, in the manufacture of most valve regulated lead acid (VRLA) batteries, low-antimony and lead–calcium alloys are still widely used as the materials for positive grids [1–4]. Sb added to Pb alloy can effectively improve the charge–discharge performance of lead-acid batteries, but it can also decrease the overpotential of the hydrogen evolution on lead alloys owing to the transference of the antimony during charging, which can lead to early excessive water loss and increase the self-discharge for the VRLA battery [5,6]. Compared with Sb, Ca added to Pb alloys can decrease the water loss of the batteries, which is helpful for batteries to have a rather good maintenance-free performance. However, corrosion at the grain boundaries occurs between the crystal grains in the Pb–Ca alloy, and a high-resistivity oxide corrosion layer forms on the Pb–Ca alloy during charging, which can give rise to a bad influence on the deep charge–discharge cycles of the batteries [7,8].

Owing to the mentioned detrimental influences of Pb–Sb and Pb–Ca alloys, in the last several decades there have been numerous research papers on lead and lead alloys to choose a suitable additive of alloys and to improve their performance [4,5,9–12], e.g. Sn, Bi, Sr, Cd, and Ag.

It has been demonstrated that Sn as an additive to the Pb–Ca alloy can effectively improve the Pb–Ca alloy performance [13]. Hence, the Pb–Ca–Sn alloy has been widely used for the grid materials of the VRLA battery [9]. Although the addition of Sn can reduce the resistivity of the anodic lead oxide films to some extent, the growth of the high resistivity layer on the Pb–Ca alloy cannot be essentially eliminated owing to the presence of calcium in the alloy. Thus, the performance of Pb–Ca–Sn alloy is still not satisfactory [14].

In order to overcome the detrimental influence of Pb–Sb and Pb–Ca alloys, we attempted to research and develop some new lead alloys instead of the lead alloys containing Sb or Ca. In previous work we discovered that some rare-earth elements, such as Ce added to Pb–Ca–Sn alloy can inhibit the corrosion of the alloy at the deep discharge potential of 0.9 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) and decrease the resistance of the anodic Pb(II) film significantly [15]. As Sm and Ce have similar properties, we studied the Pb–Sm–Sn alloy as the

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positive grid material and compared it with the Pb–Ca–Sn alloy in this work.

2. Experimental

2.1. Electrochemical measurements

A proprietary Pb–0.73 wt.% Sm–0.63 wt.% Sn alloy [16] (Pb–Sm–Sn) rod and a conventional Pb–0.088 wt.% Ca–0.63 wt.% Sn alloy (Pb–Ca–Sn) rod were used as working electrodes. The alloys were manufactured by the Shanghai Powerson Power Supply Co. with lead (99.99%), samarium (99.9%), calcium (99.9%) and tin (99.9%), and mixed using a vacuum fusion method [16]. The rods were sealed with epoxy resin in the lower part of an L-shaped glass tube, so that a cross-sectional area of 0.2–0.3 cm² was exposed in the electrolyte. A flat working-electrode surface was obtained by mechanical polishing with emery paper of successively decreasing grain size down to about 10 μm. The working electrode was then washed with double-distilled water before being immersed in the electrolyte. Before the experiment, a cathodic polarization at a potential of –1.2 V for 20 min was performed in order to remove any oxidation products formed by aerial oxidation during preliminary treatment. The electrolyte was 4.5 mol dm^{–3} H₂SO₄ solution prepared from A.R. H₂SO₄ and double-distilled water. A platinum plate served as a counter electrode. An Hg/Hg₂SO₄ electrode containing the same solution in the electrochemical cell was used as the reference electrode. All potentials reported here were referred to this electrode.

The linear sweep voltammetry (LSV) was performed using a CH Instrument model 633 Electrochemical Working Station. The working electrode was polarized at 1.28 V (near the potential of the positive grid at floating charge) for 1 h, then the potential was swept from 1.28 to 0.9 V at a rate of 1 mV s^{–1}.

Impedance–time curves were recorded using a CH Instrument model 660 Electrochemical Working Station with a frequency of 1000 Hz. While the corrosion layer was grown at the floating charge potential of 1.28 V, the change of the real part of the impedance (*Z'*) for the anodic film with the time was measured.

Cyclic voltammetry (CV) was carried out using a CH Instrument model 660 Electrochemical Working Station. The potential applied to the working electrode was between 0.6 and 1.6 V (1.6 V is near that of the positive grid at equalizing charge), and the potential scanning rate was 5 mV s^{–1}.

All electrochemical measurements were performed at 25 ± 1 °C.

2.2. Battery life test

Two similar types of 2V–200Ah VRLA batteries (i.e. one with Pb–Sm–Sn positive grids, and the other with Pb–Ca–Sn positive grids) used as communication power sources were

manufactured by the Shanghai Powerson Power Supply Co. The accelerating life test of the batteries at a floating voltage of 2.25 V and temperature of 60 °C was performed. After the initial capacities were measured, the batteries were kept at the floating charge voltage (2.25 V) for 3 months. At the end of 3 months, the capacities of the batteries were measured again. Then measurements of capacity were taken every month. During capacity testing, the batteries were discharged at a 10-h rate (20 A) until the end of discharge when the voltage was 1.8 V.

3. Results and discussion

3.1. Linear sweep voltammetry (LSV)

Fig. 1 shows the voltammograms of the anodic films formed on the Pb–Sm–Sn and Pb–Ca–Sn alloys at the floating charge potential of 1.28 V for 1 h. In Fig. 1, peak a (1.07 V) corresponds to the reduction of β-PbO₂ to PbSO₄ [17]. Peak b (1.03 V) is caused by the oxidation of a small amount of Pb(II) to α-PbO₂ [18].

Table 1 lists the reduction charges of peak a (*Q_a*) of the two alloy electrodes in Fig. 1. It can be seen from Table 1 that the *Q_a* of the Pb–Sm–Sn (29.3 mC cm^{–2}) is smaller than that of the Pb–Ca–Sn (47.3 mC cm^{–2}). Evidently the main corrosion product formed on the lead alloy surface at 1.28 V is β-PbO₂ [17]. Therefore, it can be concluded that Sm added to the lead alloy can more effectively inhibit the growth of the anodic PbO₂ film.

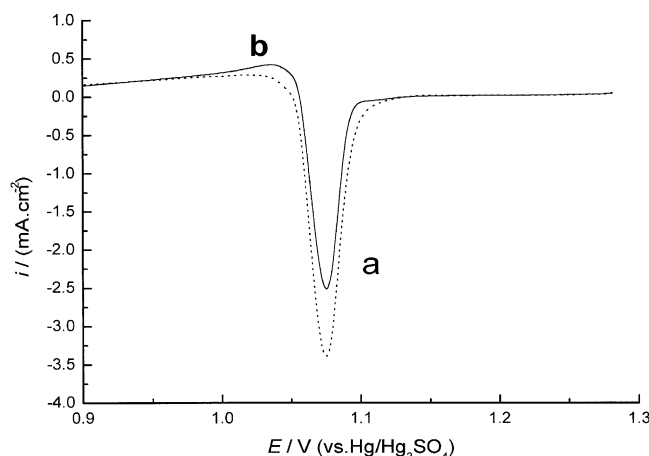


Fig. 1. Voltammograms of anodic films formed on Pb–Sm–Sn and Pb–Ca–Sn alloys at 1.28 V in 4.5 mol dm^{–3} H₂SO₄ solution for 1 h ($v = 1 \text{ mV s}^{-1}$): —, Pb–Sm–Sn; ···, Pb–Ca–Sn.

Table 1

The reduction charges of peak a (*Q_a*) of Pb–Sm–Sn and Pb–Ca–Sn alloys

Alloys	<i>Q_a</i> (mC cm ^{–2})
Pb–Sm–Sn	29.3
Pb–Ca–Sn	47.3

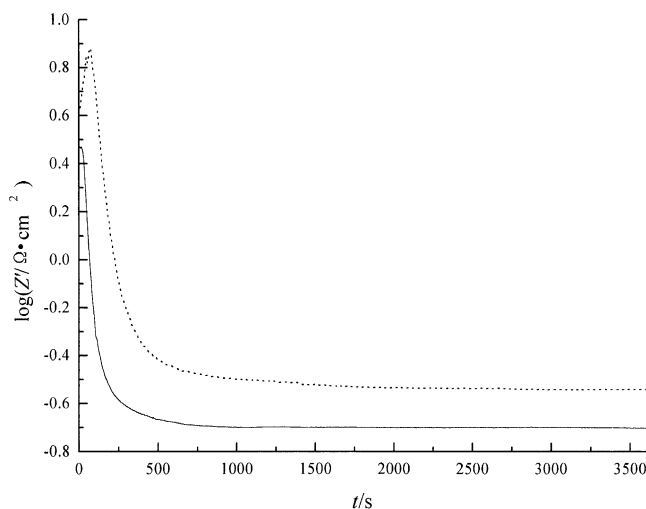


Fig. 2. Log Z' - t curves of Pb-Sm-Sn and Pb-Ca-Sn alloy electrodes at 1.28 V for 1 h ($f=1000$ Hz): —, Pb-Sm-Sn; ···, Pb-Ca-Sn.

3.2. Log Z' -time curve

Fig. 2 shows the plots of the logarithm of the real part of the impedance ($\log Z'$) versus time (t) for the Pb-Sm-Sn and Pb-Ca-Sn alloy electrodes at 1.28 V in 4.5 mol dm⁻³ H₂SO₄ solution. From Fig. 2 it can be found that at the initial stage the value of $\log Z'$ of the Pb-Sm-Sn alloy decreases greatly with time. This corresponds to the transformation process of the low conductive PbSO₄ to the high conductive PbO₂ [17]. However, at the initial stage the value of $\log Z'$ of the Pb-Ca-Sn increases slightly before it decreases greatly with time. This corresponds to the surface passivation of PbSO₄ [17]. After a certain time (approx. 500 s), the values of $\log Z'$ of the two alloy electrodes all reach their stable state. This indicates that PbO₂ has fully covered the surfaces of the electrodes, and grows constantly at a certain rate. The later stage is closer to the state when the battery is working. Since the resistance of PbO₂ is quite low, the value of $\log Z'$ of PbO₂ is rather small at 1.28 V in Fig. 2 [19], i.e. the values of Z' for the Pb-Sm-Sn and Pb-Ca-Sn alloys are 0.198 and 0.288 Ω cm², respectively.

By comparing the similar values of the ratios of Q_a and Z' in Table 2 (i.e. Q_a (Pb-Sm-Sn)/ Q_a (Pb-Ca-Sn) and Z' (Pb-Sm-Sn)/ Z' (Pb-Ca-Sn) are 0.620 and 0.688, respectively), it may be concluded that the anodic PbO₂ film on the Pb-Sm-Sn alloy is thinner than that on the Pb-Ca-Sn alloy. Therefore, it can be suggested that the performance of the VRLA batteries with the Pb-Sm-Sn alloy positive grids

Table 2
 Q_a and Z' for Pb-Sm-Sn and Pb-Ca-Sn alloys

	Q_a (mC cm ⁻²)	Z' (Ω cm ²)
Pb-Sm-Sn	29.3	0.198
Pb-Ca-Sn	47.3	0.288
Q_a (Pb-Sm-Sn)/ Q_a (Pb-Ca-Sn)	0.620	—
Z' (Pb-Sm-Sn)/ Z' (Pb-Ca-Sn)	—	0.688

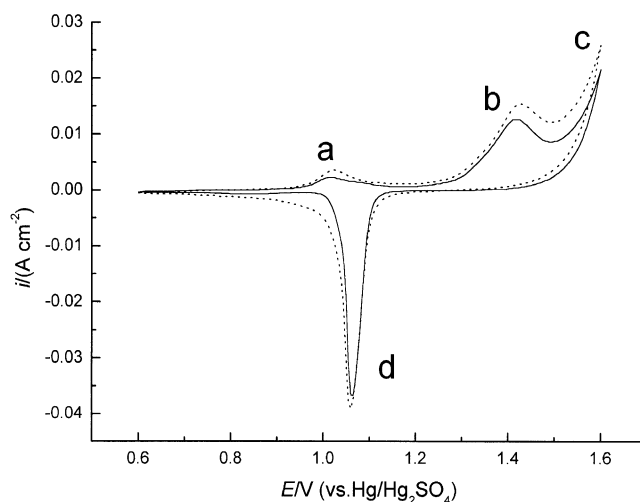


Fig. 3. Cyclic voltammograms at 30th cycle of Pb-Sm-Sn and Pb-Ca-Sn alloy electrodes in 4.5 mol dm⁻³ H₂SO₄ solution ($v=5$ mV s⁻¹): —, Pb-Sm-Sn; ···, Pb-Ca-Sn.

may be superior to that with the Pb-Ca-Sn alloy positive grids.

3.3. Cyclic voltammetry (CV)

Fig. 3 shows the cyclic voltammograms of the Pb-Sm-Sn and Pb-Ca-Sn alloy electrodes in 4.5 mol dm⁻³ H₂SO₄ solution for the 30th cycle carried out between 0.6 and 1.6 V at a sweep rate of 5 mV s⁻¹. In the positive sweep, three anodic peaks (a, b, and c) can be observed; they correspond to the oxidation of Pb to Pb(II) oxides and Pb(IV) oxides, the formation of β-PbO₂ from PbSO₄ and the evolution of oxygen, respectively [20]. In the negative sweep, the cathodic peak d can be observed, which corresponds to the reduction of β-PbO₂.

The charges of evolution of oxygen can be considered as the difference between the anodic oxidation charges (Q_{ox}) and the cathodic reduction charges (Q_{red}). Table 3 lists Q_{ox} , Q_{red} , and ($Q_{ox} - Q_{red}$) at the 75th cycle. In Table 3, the value of ($Q_{ox} - Q_{red}$) for the Pb-Sm-Sn alloy is smaller than that for the Pb-Ca-Sn alloy. It can be concluded that the rate of oxygen evolution at the Pb-Sm-Sn electrode is lower than that at the Pb-Ca-Sn electrode.

Table 4 lists the Q_{red} of Pb-Sm-Sn and Pb-Ca-Sn at different cycles and the increase rates of Q_{red} of the two alloy electrodes. The result shows that the substitution of Sm for Ca in the lead alloy can decrease the growth rate of the anodic corrosion PbO₂ layer.

Table 3
Anodic oxidation charges (Q_{ox}) and cathodic reduction charges (Q_{red}), at the 75th cycle for Pb-Sm-Sn and Pb-Ca-Sn alloy electrodes

	Pb-Sm-Sn	Pb-Ca-Sn
Q_{ox} (mC cm ⁻²)	945	1099
Q_{red} (mC cm ⁻²)	432	511
($Q_{ox} - Q_{red}$) (mC cm ⁻²)	513	588

Table 4
Cathodic reduction charges (Q_{red}) for Pb–Sm–Sn and Pb–Ca–Sn alloy electrodes at different cycles

Cycles (N)	Q_{red} (mC cm^{-2})	
	Pb–Sm–Sn	Pb–Ca–Sn
15	144	161
30	182	230
45	257	314
60	335	408
75	432	511
Increasing rate ($\text{mC cm}^{-2} \text{N}^{-1}$)	4.86	5.85
Correlation coefficient between Q_{red} and N	0.990	0.997

Table 5
The capacity of the batteries at different floating charge times (60°C)

Time/month	Capacity/Ah	
	Pb–Sm–Sn positive grid	Pb–Ca–Sn positive grid
Initial	233.2	236.6
3	208.4	168.2
4	204.4	164.0
5	188.4	148.2
6	178.4	138.8
7	175.4	115.1
8	178.4	113.3
9	183.2	51.89
10	182.0	–
11	170.0	–
12	151.6	–

3.4. Battery life test

The accelerated life tests of the 2V-200Ah VRLA batteries with the Pb–Sm–Sn and Pb–Ca–Sn alloys for positive grids separately have been performed at 60°C . After the initial discharge–charge cycle, the batteries were kept at the floating charge voltage (2.25 V) for different lengths of time between 3 and 12 months and then the batteries were discharged to 1.8 V at 20 A (10-h rate) so as to measure their capacities.

Table 5 lists the capacities of the batteries with the Pb–Sm–Sn and Pb–Ca–Sn alloys for the positive grids, separately, at different floating charge times (60°C). It can be found from Table 5 that after 3 months the capacity loss of the battery with the Pb–Sm–Sn positive grids is significantly less than that with the Pb–Ca–Sn positive grids, and the life of the battery with the Pb–Sm–Sn positive grids is longer than that with the Pb–Ca–Sn positive grids.

4. Conclusions

Samarium as the substitute for the calcium in the Pb–Ca–Sn alloy can inhibit the growth of the anodic corrosion

layer (PbO_2) and reduce the impedance of the anodic corrosion layer (PbO_2) formed on the lead alloy. Moreover, the rate of the oxygen evolution at the Pb–Sm–Sn alloy is also lower than that at the Pb–Ca–Sn alloy.

The capacity loss of the battery with the Pb–Sm–Sn positive grids is significantly less than that of the battery with the Pb–Ca–Sn positive grids and the life of the battery with the Pb–Sm–Sn positive grids is longer than that with the Pb–Ca–Sn positive grids.

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References

- [1] D. Pavlov, in: B.D. McNicol, D.A.J. Rand (Eds.), *Power Sources for Electric Vehicles*, Elsevier, Amsterdam, 1984, pp. 228–245.
- [2] J.A. Bialacki, N.A. Hampson, F. Wilson, *J. Appl. Electrochem.* 15 (1985) 99.
- [3] R.-L. Cui, S.-G. Wu, *J. Power Sources* 46 (1993) 327.
- [4] H.-T. Liu, C.-X. Yang, H.-H. Liang, J. Yang, W.-F. Zhou, *J. Power Sources* 103 (2002) 173.
- [5] T. Hirasawa, K. Sasaki, M. Taguchi, H. Kaneko, *J. Power Sources* 85 (2000) 44.
- [6] B.K. Mahato, J.L. Strebe, D.F. Wilkinson, K.R. Bullock, *J. Electrochem. Soc.* 132 (1985) 19.
- [7] J.L. Caillerie, L. Albert, *J. Power Sources* 67 (1997) 279.
- [8] H. Giess, *J. Power Sources* 53 (1995) 31.
- [9] D. Slavkov, B.S. Haran, B.N. Popov, F. Fleming, *J. Power Sources* 112 (2002) 199.
- [10] H.-Y. Chen, L. Wu, C. Ren, Q.-Z. Luo, Z.-H. Xie, X. Jiang, *J. Power Sources* 95 (2001) 108.
- [11] L.T. Lam, N.P. Haigh, D.A.J. Rand, *J. Power Sources* 88 (2000) 11.
- [12] E. Hilali, L. Bouirden, *Ann. Chim. Sci. Mater.* 25 (2000) 91.
- [13] N. Bui, P. Mattesco, P. Simon, J. Steinmetz, E. Rocca, *J. Power Sources* 67 (1997) 61.
- [14] M.A. Dasoyan, I.A. Aguf, *Current Theory of Lead-Acid Batteries*, Energy Press, Leningrad, 1975, Ch. 3 (in Russian).
- [15] H.-T. Liu, J. Yang, H.-H. Liang, J.-H. Zhuang, W.-F. Zhou, *J. Power Sources* 93 (2001) 230.
- [16] H.-T. Liu, A.-S. Wang, Y.-B. Zhou, H.-Y. Fan, M. Ma, H. Zhou, Chinese Patent, Application Number 02136759.0, 2002.
- [17] J.L. Dawson, in: A.T. Kuhn (Ed.), *The Electrochemistry of Lead*, Academic Press, London, 1979, pp. 309–353.
- [18] Y.-Q. Wan, Q.-Z. Wang, H.-T. Liu, J.-H. Zhuang, W.-F. Zhou, *J. Electroanal. Chem.* 414 (1996) 159.
- [19] W. Mindt, *J. Electrochem. Soc.* 116 (1969) 1076.
- [20] H.-T. Liu, C.-X. Yang, H.-H. Liang, J. Yang, W.-F. Zhou, *Electrochemistry* 7 (2001) 439.